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The Conformation of Non-Aromatic Ring Compounds LXXI.* The Crystal and Molecular Structure of 3β-*p*-Bromobenzoyloxyandrost-5-en-17-one at 20 and –180° C

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The crystal and molecular structure of the steroid 3β-*p*-bromobenzoyloxyandrost-5-en-17-one, $C_{26}H_{31}O_3Br$, has been determined by single-crystal X-ray techniques at 20 and −180°C. The compound crystallizes in the space group $P2_1$ with two molecules per unit cell. The lattice constants at 20°C are $a=17{\cdot}566$ (8), $b=8{\cdot}360$ (10), $c=7{\cdot}838$ (4) Å, $\beta=102{\cdot}71$ (4)° and at −180°C: $a=17{\cdot}433$ (3), $b=8{\cdot}257$ (10), $c=7{\cdot}769$ (4) Å, $\beta=102{\cdot}08$ (5)°. Initial values of the positional parameters of the non-hydrogen atoms were derived from a Patterson map based upon eye-estimated photographic data, collected at −180°C using Cu $K\alpha$ radiation. Refinement of positional and vibrational parameters of the non-hydrogen atoms resulted in an R value of 0·112. The room-temperature structure was derived from absorption-corrected diffractometer data using Mo $K\alpha$ radiation. In this case parameters of all atoms were refined resulting in a final R value of 0·049. The estimated standard deviations of bond lengths and valency angles were of the order of 0·01 Å and 0·5° respectively (at room temperature). Rigid-body corrections for thermal motion have been applied to the positional parameters at 20°C. No significant differences between the molecular structures at the two temperatures are observed. The rings *A* and *C* of the steroid skeleton have the chair conformation while ring *B* is a distorted 'half chair'. Ring *D* is a nearly ideal 'half chair'. The conformational features of the title compound are compared with those of its 13α-isomer: 3β-*p*-bromobenzoyloxy-13α-androst-5-en-17-one.

Introduction

The steroid 3β-*p*-bromobenzoyloxyandrost-5-en-17-one (Fig. 1) has the normal 8β, 9α, 10β, 13β, 14α-configuration implying that the rings in the steroid skeleton are connected in the *trans* position. The X-ray analysis of the 13α-isomer with *cis* fusion of the rings *C* and *D* has been reported previously (Portheine & Romers, 1970). The investigation described in this paper was undertaken in order to compare the molecular structures of the title compound and its 13α-isomer. The experiments started with the Weissenberg technique at low temperature. Meanwhile an automatic diffractometer became available and it was decided to repeat the measurements with this instrument at room temperature, in order to compare the molecular conformations at two temperatures.

Experimental

The compound 3β-*p*-bromobenzoyloxyandrost-5-en-17-one (hereafter BPBA) is obtained from solution in acetone in the form of colourless monoclinic crystals. The crystals are elongated in the [010] direction (setting with *b* axis unique) and have {100} and {001} as principal faces.

Photographic data

The photographic intensity data were collected at −180°C (Altona, 1964) with the equi-inclination Weissenberg method using Ni-filtered Cu $K\alpha$ radiation.

The unit-cell dimensions (see Table 1) were determined with the aid of zero-layer photographs, taken from crystals mounted about [010] and [011]. Calibration was performed by means of superposed Al-powder lines [a(Al)$=4{\cdot}0492$ Å at 20°C].

The observed density at 20°C (see Table 1) corresponds with two molecules per unit cell. Absence of odd reflexions $0k0$ indicates the space group $P2_1$ or $P2_1/m$. The latter was excluded since the compound is optically active.

Non-integrated intensity data were obtained from the crystals already mentioned, with the multiple-film technique. Intensities from eight levels about [010] ($k=0$ up to 7) and three levels about [011] ($k+l=0$ up to 2) were estimated visually. Reduction to structure factor moduli (F_o and F' for observed and unobserved reflexions) was performed as described earlier (Portheine & Romers, 1970). No correction for absorption was applied. The [011] data were employed in the determination of scaling factors for the *b* axis levels according to the method of Rae (1965) and discarded afterwards.

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[*] Part LXX: Buys, H. R. & Geise, H. J. (1970). *Tetrahedron Letters*, **34**, 2991.

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2262 *b*-axis reflexions were collected including 225 non-observed reflexions.

Diffractometer data

A second set of intensity data was measured at 20°C with Zr-filtered Mo $K\alpha$ radiation by means of an automatic three-circle single-crystal diffractometer. According to the classification rules of Arndt & Willis (1966) the goniostat has normal-beam equatorial diffraction geometry, with χ-motion restricted between 0 and $-90°$. The detection is performed by means of a scintillation counter, equipped with a pulse-height discriminator.

The lattice constants at room temperature (see Table 1) were determined from a crystal mounted about [010].

For the intensity measurements a cut crystal was mounted about the normal of $(\bar{1}02)$. The intensities were measured with the moving-crystal moving-counter method (2θ-scan), the scan range lying symmetrically about the calculated reflexion position. Background counts during the half scan time were recorded at the ends of the scan range. Attenuation filters in the primary beam were used preventing the count rate from rising above 2000 c.p.s. The pulse-height discriminator was set for a 95% window centered on the Mo $K\alpha$ peak.

Reduction of observed intensities to structure factor moduli (F_o's) was carried out as follows:

$$F_o = [(S - B_1 - B_2)\,(\mathrm{Lp})^{-1} f\, A'\, M]^{1/2}\,.$$

S is the scan count and B_1 and B_2 are the background counts. The Lorentz–polarization factor is denoted by Lp and the attenuation factor by f. The absorption factor A' is calculated according to the Monte-Carlo method as proposed by de Graaff (1972). M is applied as a correction for the decrease of standard-reflexion intensities during the measuring period. The resulting estimated standard deviation (e.s.d.) of F_o is $\sigma(F_o)$.

When the observed count rate at the reflexion position was smaller than 60 c.p.s., no intensity measurement was executed. Reflexions with measured intensity $(S - B_1 - B_2)$ less than twice the standard deviation from counting statistics: $(S + B_1 + B_2)^{1/2}$, were classified as unobserved. Since the smallest measured intensities were just above 110 counts and had associated standard deviations of the order of 45–55 counts, a threshold value of 95 counts with standard deviation of 45 counts was assigned to the class of unobserved reflexions. The structure factor moduli F' and standard deviations $\sigma(F')$ were calculated as follows:

$$F' = [95\,(\mathrm{Lp})^{-1}\,A'\,M]^{1/2} \text{ and } \sigma\,(F') = (\tfrac{1}{2})F'(45/95)\,.$$

The number of these unobserved reflexions was 1529. Altogether 3340 reflexions were recorded.

Refinement

Photographic data

Owing to the symmetry $2/m$ of the Patterson function, its vector map must contain two enantiomorphic images of the molecule viewed from the bromine atom.

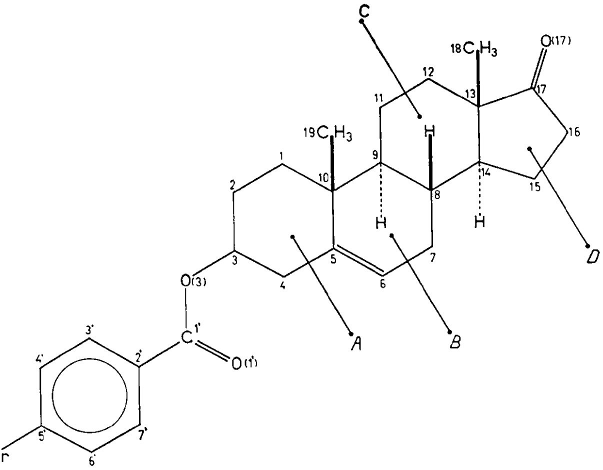

Fig. 1. Numbering of atoms and marking of the steroid rings in 3β-*p*-bromobenzoyloxyandrost-5-en-17-one (IUPAC-IUB 1969).

Table 1. *Diffraction data of BPBA*

The numbers in brackets are estimated standard deviations in terms of the last decimal given.

3β-*p*-Bromobenzoyloxyandrost-5-en-17-one, molecular composition: $C_{26}H_{31}O_3Br$, $M = 471{\cdot}4$ g. mole^{-1}, melting point 210–213°, space group $P2_1$, $Z = 2$ molecules per unit cell, $F(000) = 492$ electrons.

	Diffractometer data	Photographic data
Temperature	20°C	−180°C
λ	0·71069 Å	1·54178 Å
a	17·566 (8)	17·433 (3)
b	8·360 (10)	8·257 (10)
c	7·838 (4)	7·769 (4)
β	102·71 (4)°	102·08 (5)°
ϱ_{obs}	1·397 (7) g.cm^{-3}	–
ϱ_{calc}	1·394	1·431 g. cm^{-3}
V_{cell}	1123 Å^3	1094 Å^3
μ	19·7 cm^{-1}	30·3 cm^{-1}
Crystal size	0·4 × 0·3 × 0·1 mm	0·4 × 0·2 × 0·2 mm
Number of possible independent reflexions	4140 (up to $\theta = 30°$)	3930
Number of collected independent reflexions	3340	2262

Table 2. *Positional coordinates in fractions of the cell edges* ($\times 10^4$) *of the non-hydrogen atoms in BPBA*

Associated e.s.d.'s ($\times 10^4$) are added in brackets. Values in the first column result from photographic data at -180°C and in the second from diffractometer data at 20°C.

	x		y		z	
C(1)	−930 (6)	−932 (3)	−1062 (17)	−999 (8)	2268 (14)	2247 (7)
C(2)	−164 (6)	−169 (3)	−624 (16)	−590 (8)	3562 (15)	3512 (7)
C(3)	508 (6)	493 (3)	−391 (17)	−374 (7)	2591 (15)	2602 (6)
C(4)	302 (6)	297 (3)	821 (17)	859 (8)	1117 (15)	1133 (7)
C(5)	−464 (6)	−475 (3)	452 (12)	483 (7)	−108 (16)	−101 (6)
C(6)	−512 (5)	−529 (3)	360 (13)	413 (7)	−1829 (15)	−1824 (7)
C(7)	−1263 (5)	−1270 (3)	118 (20)	192 (9)	−3169 (12)	−3150 (6)
C(8)	−1995 (6)	−1986 (3)	345 (19)	379 (7)	−2395 (14)	−2413 (6)
C(9)	−1866 (6)	−1873 (3)	−526 (15)	−493 (7)	−602 (15)	−649 (6)
C(10)	−1172 (5)	−1178 (3)	163 (17)	215 (8)	741 (14)	735 (6)
C(11)	−2632 (6)	−2618 (3)	−677 (18)	−634 (8)	91 (16)	50 (7)
C(12)	−3343 (6)	−3326 (3)	−1302 (17)	−1296 (9)	−1310 (17)	−1297 (8)
C(13)	−3462 (6)	−3458 (3)	−287 (19)	−256 (9)	−2882 (15)	−2928 (6)
C(14)	−2708 (6)	−2710 (3)	−287 (16)	−255 (9)	−3646 (14)	−3662 (6)
C(15)	−2978 (6)	−2970 (3)	448 (16)	459 (9)	−5479 (15)	−5490 (7)
C(16)	−3816 (6)	−3798 (3)	−203 (28)	−215 (13)	−6127 (15)	−6148 (7)
C(17)	−4049 (7)	−4054 (3)	−832 (18)	−829 (9)	−4501 (19)	−4525 (8)
C(18)	−3735 (7)	−3713 (4)	1474 (19)	1465 (10)	−2528 (18)	−2567 (8)
C(19)	−1395 (6)	−1400 (3)	1816 (15)	1825 (8)	1435 (16)	1432 (7)
O(17)	−4625·9 (4·9)	−4621·3 (2·4)	−1698 (14)	−1615 (7)	−4508 (14)	−4531 (7)
C(1′)	1901 (5)	1875 (3)	−51 (20)	−16 (10)	3642 (13)	3640 (6)
C(2′)	2512 (5)	2488 (3)	107 (18)	129 (8)	5317 (13)	5292 (6)
C(3′)	2326 (6)	2309 (3)	117 (20)	137 (9)	6945 (15)	6938 (7)
C(4′)	2909 (6)	2897 (3)	79 (24)	110 (10)	8471 (14)	8421 (7)
C(5′)	3688 (6)	3661 (3)	72 (22)	87 (10)	8285 (13)	8273 (7)
C(6′)	3881 (5)	3856 (3)	94 (24)	106 (11)	6651 (14)	6682 (8)
C(7′)	3305 (6)	3266 (3)	119 (21)	131 (10)	5147 (14)	5180 (7)
O(3)	1164·1 (3·5)	1157·4 (1·8)	109 (14)	112 (6)	3977 (9)	3969 (4)
O(1′)	2027·0 (4·0)	2005·1 (2·2)	−279 (12)	−253 (8)	2219 (10)	2224 (5)
Br	4497·3 (0·6)	4471·1 (0·3)	0·0 (3·6)	0·0 (1·9)	10330·1 (1·4)	10318·3 (0·8)

In fact the images of the steroid skeleton could be distinguished separately. The *p*-bromobenzoyl group is approximately directed perpendicular to [010] and, consequently gives one image. Trial values for the positional parameters of all non-hydrogen atoms could be determined for the expected configuration of the molecule. The origin was fixed by the choice: $y(\text{Br})=0$.

Because of the $2/m$ ambiguity, the refinement was started in full-matrix version using the photographic *b*-axis data. The refined parameters were positional coordinates and individual B values of the heavy atoms together with 8 scaling factors for the reciprocal levels. The atomic scattering factors of carbon [C(valence)] and oxygen were taken from *International Tables for X-ray Crystallography* (1962) and of bromine from Cromer & Waber (1965). For hydrogen the scattering factor values of Stewart, Davidson & Simpson (1965) were used.

The function $\sum w(F_o)\,[F_o-F_c/S(F_o)]^2$ was minimized. In this expression F_c is the modulus of the calculated structure factor (on absolute scale), $S(F_o)$ the scale factor of F_o and $w(F_o)$ the weight of F_o. The summation includes the observed reflexions and the unobserved ones which have $F_c/S(F') > F'$. Twenty-five hydrogen atoms [except those at C(18) and C(19)] at fixed positions with B values of 1·9 Å^2 were contributing to F_c. In the calculation of these positions a bond distance between carbon and hydrogen atoms of 1·0 Å was assumed. Convergence of the isotropic refinement was reached at a value of 0·174 of the conventional R index: $R=\sum|F_o-F_c/S(F_o)|/(\sum F_o)$ (observed reflexions only). The following weight scheme was determined empirically: $w(F_o>1\cdot50)=(4\cdot00+F_o+F_o^2)^{-1}$, $w(F_o\le 1\cdot50)=0\cdot129$ and $w(F')=0\cdot14$.

The refinement was continued in block-diagonal approximation allowing for anisotropic vibration. A 2×2 block was used for one overall scale factor and B value while the positional and vibrational parameters of each atom were combined in a 9×9 block. No attempt was made to establish the absolute configuration of the molecule.

The final values of the positional parameters are listed in Table 2. Owing to systematic errors such as absorption and spot shape effects, the physical meaning of the vibrational parameters* is doubtful. This is expressed by the fact that the determinants of the U_{ij} tensors for the atoms C(5), C(6) and C(7) are not positive. The shifts of the final parameter values were less than one tenth of the e.s.d.'s. In the last cycle 48 unobserved reflexions were included. The R value was 0·112.

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* A list of U_{ij} values based upon the photographic data as well as the final list of observed and calculated structure factors is given elsewhere (Portheine, 1971).

Diffractometer data

The positional parameter values of the non-hydrogen atoms from the isotropic stage of the previous refinement were used as starting values in the refinement based upon the diffractometer data. The specifications were the same as before, unless mentioned explicitly. At the beginning the weight function was $w(F)=1/\sigma(F)^2$, where F stands for F_o or F'. All hydrogen atoms were included with fixed positional coordinates and with B values of 4·0 Å^2. The methyl hydrogen atoms were assumed to be in staggered conformation about the bonds C(18)–C(13) and C(19)–C(10) with respect to the atoms bound to C(13) and C(10). The minimum R value at the isotropic stage was 0·199.

A subsequent difference map revealed remarkable anisotropy for the non-hydrogen atoms. In order to determine the absolute configuration of the molecule in the next stage, the real part of the anomalous scattering factor of bromine, $\Delta f'(\mathrm{Br})=-0{\cdot}21$ electron (Cromer, 1965) was accounted for in the following anisotropic refinement.

After convergence was reached ($R=0{\cdot}0582$), structure factor lists were evaluated for the assumed structure and its inverse, using $\Delta f''(\mathrm{Br})=2{\cdot}68$ electrons. The respective R values of 0·0640 and 0·0657 can be considered to be an indication that the configuration hitherto assumed is the correct one. Afterwards the values of $\Delta f'(\mathrm{Br})$ and $\Delta f''(\mathrm{Br})$ were employed.

After a few cycles a difference map was calculated without the hydrogen atoms contributing to F_c. All these atoms could be located; those at C(18) and C(19) had approximately staggered positions (see Fig. 2). The vaguest peak corresponded with H(18,3),† which atom proved to have the highest B value (8·6 Å^2, see Table 3) at the end of the refinement. It was decided to refine the positional and isotropic vibrational parameters of the hydrogen atoms, simultaneously with the heavy-atom parameters in 4 × 4 blocks.

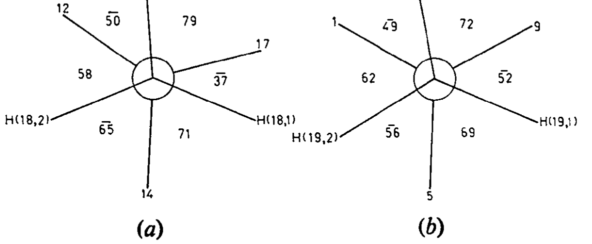

Fig. 2. Newman projections along the bonds (*a*) C(18)–C(13) and (*b*) C(19)–C(10) of BPBA (20°C) showing the approximately staggered conformations about these bonds. Numbers are values of torsional angles in degrees. The sign convention from Klyne & Prelog (1960) is adopted. A bar indicates a negative sign.

Table 3. *Fractional coordinates* (× 10^3) *and B values* (Å^2) *of the hydrogen atoms in BPBA, based upon diffractometer data*

Associated e.s.d.'s are appended in brackets.

	x	y	z	B
H(1α)	−88 (3)	−201 (6)	165 (5)	1·9 (1·0)
H(1β)	−135 (3)	−120 (7)	294 (6)	3·8 (1·2)
H(2α)	−1 (3)	−128 (6)	430 (5)	2·4 (1·0)
H(2β)	−26 (3)	27 (7)	415 (6)	4·2 (1·3)
H(3α)	63 (3)	−145 (6)	218 (6)	2·3 (1·0)
H(4α)	70 (4)	103 (9)	50 (8)	5·6 (1·5)
H(4β)	32 (3)	184 (7)	172 (7)	4·7 (1·5)
H(6)	−3 (3)	45 (6)	−232 (6)	3·4 (1·2)
H(7α)	−130 (4)	−78 (8)	−359 (8)	5·3 (1·5)
H(7β)	−132 (3)	95 (7)	−402 (6)	3·2 (1·2)
H(8β)	−207 (3)	141 (7)	−223 (6)	3·3 (1·2)
H(9α)	−174 (2)	−151 (5)	−85 (5)	1·0 (0·8)
H(11α)	−247 (3)	−139 (7)	114 (6)	3·2 (1·1)
H(11β)	−271 (2)	42 (5)	64 (5)	2·0 (1·0)
H(12α)	−319 (3)	−269 (8)	−163 (7)	5·0 (1·5)
H(12β)	−380 (3)	−116 (7)	−95 (6)	3·3 (1·2)
H(14α)	−258 (3)	−161 (7)	−367 (6)	3·7 (1·2)
H(15α)	−257 (3)	24 (7)	−636 (6)	4·0 (1·2)
H(15β)	−294 (3)	153 (7)	−533 (7)	4·0 (1·3)
H(16α)	−389 (3)	−116 (7)	−686 (7)	4·2 (1·3)
H(16β)	−419 (3)	44 (7)	−689 (7)	4·5 (1·4)
H(18,1)	−390 (4)	196 (8)	−353 (8)	5·6 (1·6)
H(18,2)	−333 (2)	198 (5)	−165 (5)	1·2 (0·9)
H(18,3)	−414 (4)	134 (11)	−198 (9)	8·6 (2·2)
H(19,1)	−160 (3)	244 (7)	44 (7)	4·0 (1·3)
H(19,2)	−102 (3)	237 (7)	222 (6)	2·7 (1·1)
H(19,3)	−175 (3)	160 (8)	216 (6)	4·0 (1·3)
H(3′)	171 (3)	38 (7)	699 (6)	3·9 (1·3)
H(4′)	272 (3)	11 (8)	955 (6)	4·8 (1·3)
H(6′)	443 (3)	10 (7)	649 (5)	3·0 (1·0)
H(7′)	339 (3)	−10 (9)	396 (6)	4·6 (1·2)

In order to obtain independence of F and $\{w(F)\,[F-F_c/S(F)]^2\}$ the modified weight function:

$$w(F)=\{[\sigma(F)]^2\,(0{\cdot}71+0{\cdot}066\,F)\}^{-1}$$

was used in the last cycles of the refinement. The shifts in the final parameter values* (see Tables 2 and 4 for positional and vibrational parameters of the non-hydrogen atoms and Table 3 for the hydrogen atom parameters) were less than one sixth of the corresponding e.s.d.'s. In the last cycle 248 unobserved reflexions were included. The final R index for the observed reflexions was $R=0{\cdot}0487$.

Thermal motion

The thermal motion of different groups of atoms has been analysed in terms of the rigid-body tensors of translation (**T**), libration (**L**) and screw motion (**S**) (Schomaker & Trueblood, 1968) using the room-temperature U_{ij} values (observed values).

Rigid-body motion of the entire molecule was tested (hydrogen atoms excluded), of the steroid part [atoms O(17) and C(1) to C(19)] and of the *p*-bromobenzoyloxy group [atoms Br, O(3), O(1′) and C(1′) to C(7′)].

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† The hydrogen atoms are indicated with the numbers of the carbon atoms to which they are attached and with their configuration at the steroid skeleton. The numbering of the methyl hydrogen atoms is shown in Fig. 2.

* The list of calculated and observed structure factor moduli and associated e.s.d.'s can be found elsewhere (Portheine, 1971).

Table 4. *Observed* (*o*) *and calculated* (*c*) U_{ij} *values of the non-hydrogen atoms in BPBA at* 20°C

The temperature factor is defined as: $\exp(-2\pi^2 \sum_{i,j} h_ih_ja_i^*a_j^*U_{ij})$. Numbers given in brackets are e.s.d.'s. Units are 10^{-3} Å^2.

	U_{11}		U_{22}		U_{33}		$2U_{12}$		$2U_{23}$		$2U_{31}$	
	o	*c*	*o*	*c*	*o*	*c*	*o*	*c*	*o*	*c*	*o*	*c*
C(1)	38 (3)	41	50 (4)	55	36 (3)	37	−13 (6)	−6	8 (5)	12	6 (4)	17
C(2)	39 (3)	46	74 (5)	66	36 (3)	37	6 (6)	−3	15 (6)	12	3 (4)	6
C(3)	36 (2)	39	44 (4)	55	40 (3)	43	−8 (5)	−3	−11 (5)	5	3 (4)	2
C(4)	41 (3)	36	54 (4)	47	42 (3)	42	−27 (6)	−13	6 (6)	−1	6 (5)	6
C(5)	35 (3)	34	42 (4)	40	35 (2)	35	−5 (5)	−9	6 (4)	−1	8 (4)	13
C(6)	33 (2)	36	48 (4)	54	42 (3)	36	−1 (5)	−14	2 (5)	2	21 (4)	18
C(7)	40 (3)	39	60 (4)	61	34 (2)	33	−2 (7)	−12	3 (6)	−3	10 (4)	17
C(8)	31 (2)	36	52 (4)	46	36 (2)	34	6 (5)	−4	−12 (5)	−6	14 (4)	11
C(9)	36 (2)	33	41 (3)	41	34 (2)	35	−2 (5)	−5	−5 (5)	−8	16 (4)	18
C(10)	30 (2)	35	46 (4)	41	33 (2)	33	0 (5)	−3	−3 (5)	−6	13 (4)	15
C(11)	36 (3)	35	62 (4)	59	36 (3)	43	−6 (5)	−7	−9 (5)	−9	13 (4)	26
C(12)	37 (3)	34	63 (4)	66	57 (4)	55	−18 (6)	−15	−20 (7)	−15	16 (5)	24
C(13)	33 (2)	34	59 (4)	64	45 (3)	50	5 (7)	−2	−28 (7)	−22	6 (4)	8
C(14)	32 (2)	37	55 (4)	59	40 (2)	39	−6 (6)	−5	−10 (6)	−16	12 (4)	7
C(15)	45 (3)	48	93 (6)	88	37 (3)	40	−19 (7)	−5	−3 (6)	−4	−8 (5)	−6
C(16)	56 (3)	47	100 (6)	102	46 (3)	50	−14 (11)	−4	−18 (9)	−25	−24 (5)	−15
C(17)	31 (3)	37	72 (5)	83	68 (4)	60	5 (6)	−8	−30 (7)	−34	7 (5)	−3
C(18)	49 (4)	39	78 (5)	70	61 (4)	62	15 (8)	21	−24 (8)	−25	12 (6)	−1
C(19)	47 (3)	43	48 (4)	50	42 (3)	43	3 (6)	6	−25 (5)	−28	20 (5)	8
O(17)	39 (2)	37	104 (4)	98	83 (3)	78	−32 (6)	−20	−57 (7)	−45	14 (5)	−1
C(1′)	37 (2)	38	47 (3)	51	50 (3)	44	−15 (7)	−6	−8 (8)	−5	7 (4)	16
C(2′)	35 (2)	33	44 (3)	39	49 (3)	47	3 (6)	−3	2 (7)	−3	12 (4)	16
C(3′)	33 (2)	34	58 (4)	60	51 (3)	45	7 (7)	0	−7 (7)	−7	15 (4)	12
C(4′)	41 (3)	41	77 (5)	76	45 (3)	48	−6 (8)	1	1 (8)	−6	14 (4)	3
C(5′)	36 (2)	37	61 (4)	61	56 (3)	60	−6 (8)	−1	−15 (8)	−2	−10 (4)	−4
C(6′)	36 (3)	32	77 (5)	73	74 (4)	69	−15 (9)	−3	1 (10)	0	23 (5)	12
C(7′)	36 (2)	34	62 (4)	67	54 (3)	58	14 (7)	−6	10 (8)	0	23 (4)	23
O(3)	30 (2)	35	69 (3)	68	40 (2)	47	−1 (5)	−3	−6 (5)	−6	2 (3)	8
O(1′)	50 (2)	50	94 (4)	91	44 (2)	46	−10 (6)	−4	−18 (6)	−14	26 (3)	23
Br	51 (0)	50	108 (1)	109	76 (0)	76	5 (1)	2	2 (1)	2	−39 (1)	−34

Table 5. *Rigid-body thermal parameters of BPBA based upon diffractometer data at* 20°C

Axes of reference are $\bar{a}$, $\bar{b}$ and $\bar{c}^*$. E.s.d.'s are given in parentheses.

Principal axes of reduced **T** [formula (20) of Schomaker & Trueblood (1968)]

	Rigid body of the atoms: O(17) and C(1) to C(19)				Rigid body of the atoms: Br, O(3), O(1′) and C(1′) to C(7′)			
	r.m.s. amplitude(Å)	Direction cosines (×10³)			r.m.s. amplitude (Å)	Direction cosines (×10³)		
	0·20	304	−877	372	0·22	−171	−223	960
	0·18	829	51	−557	0·20	261	−950	−174
	0·18	470	478	742	0·18	950	221	220

L[× 10⁻¹(°)²]

$$\begin{pmatrix} 144\ (15) & 46\ (5) & 87\ (12) \\ & 6\ (6) & 59\ (11) \\ & & 10\ (6) \end{pmatrix} \qquad \begin{pmatrix} 303\ (30) & 80\ (10) & 367\ (51) \\ & 4\ (17) & 218\ (33) \\ & & 1\ (22) \end{pmatrix}$$

Principal axes of **L**

	r.m.s. amplitude (°)	Direction cosines (×10³)			r.m.s. amplitude (°)	Direction cosines (×10³)		
L_1	4·3	842	76	534	7·5	−654	−7	−757
L_2	2·3	476	−572	−668	3·4	−755	−59	653
L_3	2·0	255	817	−518	2·8	−49	998	33

Displacement of libration axes from intersecting (Å)

$L_{1,2}=0{\cdot}15$	$L_{1,3}=-0{\cdot}17$	$L_{1,2}=-0{\cdot}07$	$L_{1,3}=0{\cdot}04$
$L_{2,1}=2{,}02$	$L_{2,3}=0{\cdot}17$	$L_{2,1}=1{\cdot}75$	$L_{2,3}=0{\cdot}22$
$L_{3,1}=-0{\cdot}83$	$L_{3,2}=0{\cdot}24$	$L_{3,1}=2{\cdot}45$	$L_{3,2}=-0{\cdot}67$

Effective screw translation (Å)

parallel to L_1	−0·015	0·000
parallel to L_2	0·013	0·000
parallel to L_3	0·016	0·001

U_{ij} values calculated on the basis of the separate rigid bodies for the two parts of the molecule (see Table 4) showed no discrepancies with the observed values, in view of the e.s.d.'s resulting from the refinement. The rigid body for the whole molecule did not yield satisfactory results. In Table 5 the rigid-body parameters for the two moieties are given.

The **T**-tensors are virtually isotropic while the **L**-tensors show prominent anisotropy. The principal directions of the **L**-tensors are indicated as L_1, L_2 and L_3. The angles between the crystallographic axes $\bar{a}$, $\bar{b}$ and $\bar{c}$ and L_1 of the steroid part are 33, 86 and 70°, indicating that this direction virtually coincides with the longitudinal axis of this moiety.

Corrections to the atomic positions were applied using a value of 0·10 Å^2 for the peak-breadth parameter (Cruickshank, 1956) of each atom. The resulting bond lengths are given in column 3 of Table 6 and in Fig. 3(*a*). The absolute values of the corrections for valency and torsional angles were in the ranges of 0·0–0·3 and 0·0–0·1 degrees. Corrected values are shown in Figs. 3(*b*) and 4(*a*) respectively. The average e.s.d.'s of the non-corrected valency and torsional angles are 0·5 and 0·7 degrees respectively.

Because of the uncertain physical meaning of the photographic vibrational parameters, no attempt was made to analyse the thermal motion in this case.

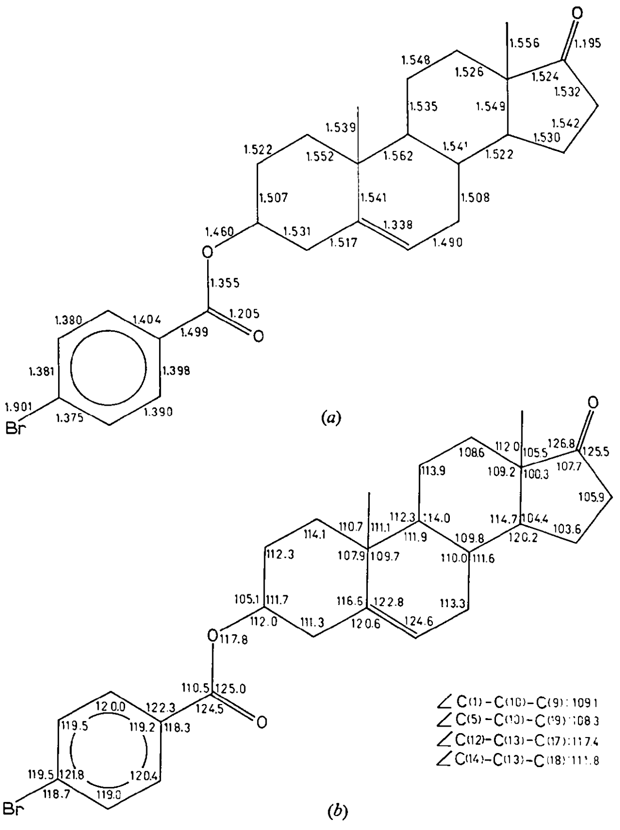

Fig. 3. (*a*) Bond lengths (Å) and (*b*) valency angles in decimal degrees in BPBA at 20 °C after correction for thermal motion.

Table 6. *Values of bond lengths* (Å) *in BPBA resulting from photographic data at* −180 °C, *from diffractometer data at* 20 °C, *and values corrected for thermal motion* resulting from the latter data*

Associated e.s.d.'s (10^{-3} Å) are appended in brackets.

	Photographic	Diffractometer	Diffractometer (corrected)
C(1)—C(2)	1·537 (15)	1·520 (7)	1·522
C(1)—C(10)	1·549 (17)	1·548 (8)	1·552
C(2)—C(3)	1·533 (15)	1·503 (8)	1·507
C(3)—C(4)	1·507 (18)	1·526 (8)	1·531
C(4)—C(5)	1·500 (15)	1·515 (7)	1·517
C(5)—C(6)	1·324 (17)	1·335 (7)	1·338
C(5)—C(10)	1·536 (14)	1·537 (7)	1·541
C(6)—C(7)	1·506 (14)	1·488 (7)	1·490
C(7)—C(8)	1·532 (15)	1·504 (7)	1·508
C(8)—C(9)	1·541 (17)	1·536 (7)	1·541
C(8)—C(14)	1·501 (16)	1·520 (7)	1·522
C(9)—C(10)	1·531 (16)	1·559 (7)	1·562
C(9)—C(11)	1·546 (15)	1·532 (7)	1·535
C(10)–C(19)	1·547 (19)	1·535 (9)	1·539
C(11)–C(12)	1·557 (17)	1·545 (8)	1·548
C(12)–C(13)	1·459 (19)	1·521 (9)	1·526
C(13)–C(14)	1·552 (15)	1·545 (7)	1·549
C(13)–C(17)	1·515 (17)	1·522 (8)	1·524
C(13)–C(18)	1·572 (21)	1·551 (11)	1·556
C(14)–C(15)	1·529 (16)	1·526 (8)	1·530
C(15)–C(16)	1·540 (16)	1·540 (9)	1·542
C(16)–C(17)	1·499 (21)	1·528 (10)	1·532
C(17)–O(17)	1·232 (16)	1·193 (8)	1·195
C(3)—O(3)	1·457 (13)	1·458 (6)	1·460
C(1′)–C(2′)	1·504 (13)	1·496 (6)	1·499
C(2′)–C(3′)	1·370 (16)	1·393 (7)	1·404
C(2′)–C(7′)	1·417 (13)	1·390 (7)	1·398
C(3′)–C(4′)	1·391 (15)	1·376 (7)	1·380
C(4′)–C(5′)	1·397 (14)	1·372 (7)	1·381
C(5′)–C(6′)	1·379 (15)	1·364 (8)	1·375
C(6′)–C(7′)	1·372 (14)	1·386 (8)	1·390
C(1′)–O(3)	1·370 (11)	1·346 (6)	1·355
C(1′)–O(1′)	1·186 (13)	1·198 (6)	1·205
C(5′)–Br	1·892 (9)	1·897 (5)	1·901

* The corrected bond lengths will have e.s.d.'s that are probably 20% higher than the e.s.d.'s of the non-corrected lengths, because of the inaccuracy of the corrections.

Discussion of the structure

In columns 1 and 2 of Table 6 the bond lengths of BPBA are listed as derived from positional coordinates at −180 and 20 °C (uncorrected values). The correlation coefficients of the positional parameters of one atom were used in the calculation of the quoted e.s.d.'s, while the inaccuracy of the attice constants was neglected.

Inspecting columns 2 and 3 of Table 6, one notes that the thermal-motion corrections of the bond lengths at 20 °C are in the range of 0·002 to 0·011 Å. If it would have been possible to apply corrections to the low-temperature positions, one would have found values of at most one third of the room-temperature corrections. One may assume therefore, that no substantial systematic effects due to thermal motion are present in the differences between the bond lengths at −180 °C and the corrected lengths at 20 °C. The equivalence of these distance sets can be accepted if one disregards the exceptionally large difference of 0·067 Å for the bond C(12)–C(13). Assuming that the e.s.d. of this difference, 0·021 Å, is a thirty per cent underestimation of the real standard deviation, one need not reject the equivalence on basis of this particular observation, if a 98·5% confidence interval is accepted. No significant differences are observed between the valency angles at the two temperatures. The corresponding e.s.d.'s are of the orders 0·9 and 0·5° for the values at −180°C and the non-corrected values at 20°C.

The observed distances (corrected values at 20°C) are in good agreement with expected values. The average value of the bond lengths between carbon atoms in the sp^3 hybridization state is 1·536 Å and the r.m.s. difference of this average with the individual values is 0·016 Å. The largest distance is observed for the bond C(9)–C(10): 1·562 Å. This value is not significantly different from the average value, but is in good agreement with the weighted mean value (1·564 Å with an *e.s.d.* of 0·001 Å) of bond lengths C(9)–C(10) observed in twenty steroid structures, irrespective of the configuration of the atoms C(9) and C(10). The weighted mean value mentioned is considerably larger than the value of 1·533 Å for the C(sp^3)–C(sp^3) distance in n-alkanes (Bonham, Bartell & Kohl, 1959). Steric overcrowding of the steroid molecule in the neighbourhood of the atoms C(9) and C(10) may be invoked to explain this enlargement.

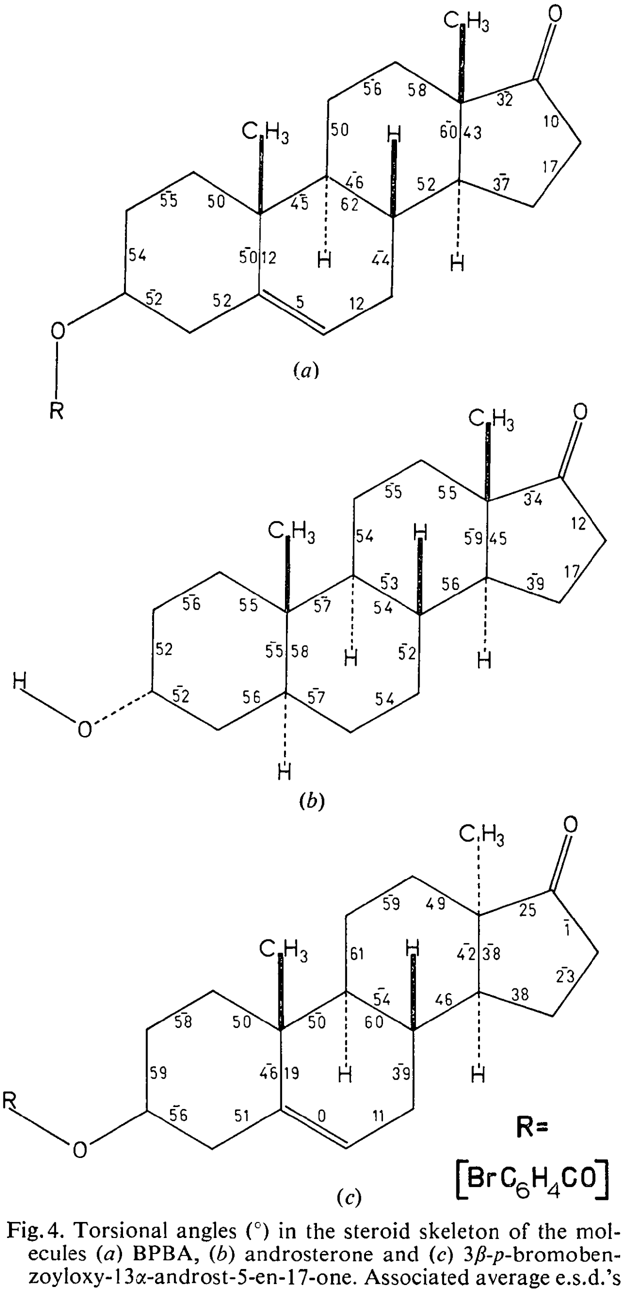

Fig. 4. Torsional angles (°) in the steroid skeleton of the molecules (*a*) BPBA, (*b*) androsterone and (*c*) 3β-*p*-bromobenzoyloxy-13α-androst-5-en-17-one. Associated average e.s.d.'s are (*a*) 1, (*b*) 1 and (*c*) 2°.

The valency angles of the *p*-bromobenzoyloxy group are normal. Since valency and torsional angles in fused cyclohexane systems are correlated, it suffices to discuss the latter.

The torsional angles at 20 and −180°C show no significant differences. The torsional angles in the steroid skeleton of the molecules BPBA (room temperature), androsterone (High & Kraut, 1966) and 3β-*p*-bromobenzoyloxy-13α-androst-5-en-17-one (Portheine & Romers, 1970) are given in Fig. 4.

The distribution of torsional angles in the rings *A* and *C* of BPBA indicates that these rings have distorted chair forms. The conformation of ring *D* in BPBA is characterized (Altona, Geise & Romers, 1968) by the values of 42·8° for the 'puckering angle' φ_m and −9·0° for the 'phase angle' δ (at −180°C: 42·5 and −6·6° respectively). The conformation of this ring does not deviate seriously from C_2 symmetry ($\delta=0°$) with the twofold axis running through the atom C(16) and the midpoint of the bond C(13)–C(14) (half-chair form). Since φ_m and δ in androsterone have virtually the same values (45·1 and −7·5° respectively) it may be concluded that introduction of the double bond C(5)–C(6) in ring *B* has no influence on the conformation of ring *D*.

Comparison of the conformations of the *B* ring in BPBA and cyclohexene in the gas phase (Chiang & Bauer, 1969; Geise & Buys, 1971) shows that ring *B* is slightly deformed in the region of the atoms C(5) and C(6) with respect to the half-chair conformation in cyclohexene. The equality of the sum of the absolute values of the torsional angles φ(7–8–9–10)* and φ(11–9–8–14) in BPBA and androsterone is in accordance with the conformation-transmission rule for *trans*-fused rings (Bucourt, 1964). The large value of 62° for φ(7–8–9–10) in BPBA, compared with androsterone, requires deformation of ring *C* in such a way that between the atoms C(12) and C(13) the puckering is increased. This requirement is partly concomitant with the demand of the *trans*-fused *D* ring for an increased puckering about C(13) and C(14) [see Fig. 5(*b*)].

In 3β-*p*-bromobenzoyloxy-13α-androst-5-en-17-one the rings *C* and *D* are connected in the *cis* position

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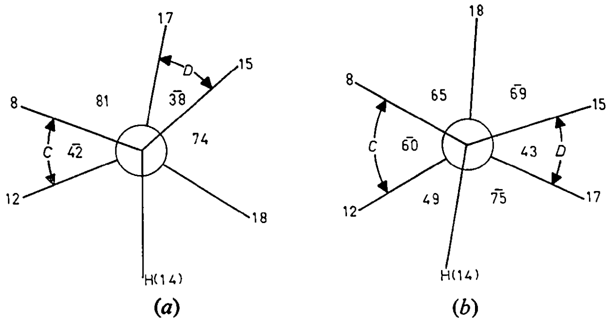
* The numbers refer to the carbon atoms concerned.

[Fig. 5(*a*)]. Accordingly (Bucourt, 1964), ring *D* requires deformation of *C* with highest puckering between C(8), C(9), C(11) and C(12) which counteracts the demand of ring *B*. The actual deformation of ring *C* is mainly influenced by ring *D* while *B* itself is somewhat distorted in the direction of a sofa form with respect to BPBA. The conformational differences between the rings *A* in the two compounds are caused by different *B* ring conformations.



(*a*) (*b*)

Fig. 5. Newman projections along the bond C(13)–C(14) of (*a*) 3β-*p*-bromobenzoyloxy-13α-androst-5-en-17-one and (*b*) BPBA. Coupling of the rings *C* and *D* in *cis* and *trans* configurations is shown.

Mean values of distances, $\langle d\rangle$ and angles, $\langle\psi\rangle$, involving hydrogen atoms, are determined from uncorrected positional parameters at 20 °C (see Table 7). The values are distinguished with respect to the hybridization state of the carbon atom to which the hydrogen atoms are bound. The r.m.s. differences of the mean values with the individual observations are compared with the average e.s.d.'s based upon the refinement. The r.m.s. differences are not in disagreement with the $\langle$e.s.d.$\rangle$ values. The observed values of H–C distances and H–C–H and H–C–C angles (sp^3 hybridization) are virtually the same as the corresponding values in androsterone (0·99 Å, 107 and 109° respectively). In the refinement of the latter compound a different hydrogen scattering factor was employed but the same block scheme was used.

Packing

The packing of the molecules at room temperature is illustrated in Fig. 6. At a distance less than 3·90 Å the reference molecule, I, (corresponding to the listed parameters) is surrounded by twelve molecules, II to XIII having the following coordinates:

I: $x, \quad y, z$;
II: $x, \quad y, z+1$;
III: $x, \quad y, z-1$;
IV: $x+1, y, z+1$;
V: $x-1, y, z-1$;
VI: $x+1, y, z+2$;
VII: $x-1, y, z-2$;
VIII: $\bar{x}, \quad y+\frac{1}{2}, \bar{z}$;
IX: $\bar{x}, \quad y-\frac{1}{2}, \bar{z}$;
X: $\bar{x}, \quad y+\frac{1}{2}, \bar{z}+1$;
XI $\bar{x}, \quad y-\frac{1}{2}, \bar{z}+1$;
XII: $\bar{x}-1, y+\frac{1}{2}, \bar{z}-1$;
XIII: $\bar{x}-1, y-\frac{1}{2}, \bar{z}-1$.

The corresponding intermolecular distances at both temperatures are listed in Table 8. No vibrational corrections have been applied.

Table 8. *Intermolecular distances* (Å) *in BPBA smaller than* 3·90 Å *at* 20 *and* −180 °C

Roman numerals are explained in the text.

	20 °C	−180 °C
C(6′),I–O(17),IV	3·35*	3·28
C(19),I–C(3′),X	3·57*	3·54
C(6),I—C(3),VIII	3·58*	3·56
C(6′),I–O(17),VIII	3·63*	3·52
C(2),I—C(7),II	3·64	3·54
C(16),I–Br, VII	3·64*	3·59
C(8),I—O(1′),VIII	3·65	3·62
C(18),I–O(17),XII	3·66*	3·60
C(4′),I–O(1′),II	3·67	3·58
C(7′),I–O(17),VIII	3·72	3·60
C(7′),I–C(17),VIII	3·73	3·66
C(4′),I–C(12),X	3·73	3·70
C(19),I–O(1′),VIII	3·74	3·70
C(11),I–C(15),II	3·79	3·73
C(4′),I–C(11),X	3·82	3·74
C(19),I–C(4′),X	3·82	3·78
C(18),I–Br,X	3·83	3·76
C(6′),I–C(17),VIII	3·85	3·79
C(4),I—C(6),VIII	3·85	3·80
Br,I——C(12),X	3·86	3·82
C(18),I–C(7′),VIII	3·86	3·79
C(6),I—C(2),VIII	3·89	3·85

* Distance is shown in Fig. 6.

The intermolecular distances at −180°C are considerably smaller than those at 20°C, which is reflected in the shrinkage of the cell at low temperature (see Table 1). Comparison of the positional parameters at the two temperatures indicates systematic differences in *x* and *y* values. Compared with the room-temper-

Table 7. *Mean values of distances*, $\langle d\rangle$ *and angles*, $\langle\psi\rangle$ *involving hydrogen atoms, derived from diffractometer data of BPBA*

The number of individual observations is *N*.

Distances (Å)		
Type	H–C	H–C
Hybridization	sp^3	sp^2
N	26	5
$\langle d\rangle=\sum_i d_i/N$	0·97	1·04
$[\sum_i (d_i-\langle d\rangle)^2/N]^{\frac{1}{2}}$	0·09	0·06
$\langle$e.s.d.$\rangle$	0·05	0·05

Angles (°)			
Type	H–C–H	H–C–C	H–C–C
Hybridization	sp^3	sp^3	sp^2
N	14	49	10
$\langle\psi\rangle=\sum_i \psi_i/N$	106	110	119
$[\sum_i (\psi_i-\langle\psi\rangle)^2/N]^{\frac{1}{2}}$	7	5	4
$\langle$e.s.d.$\rangle$	5	3	3

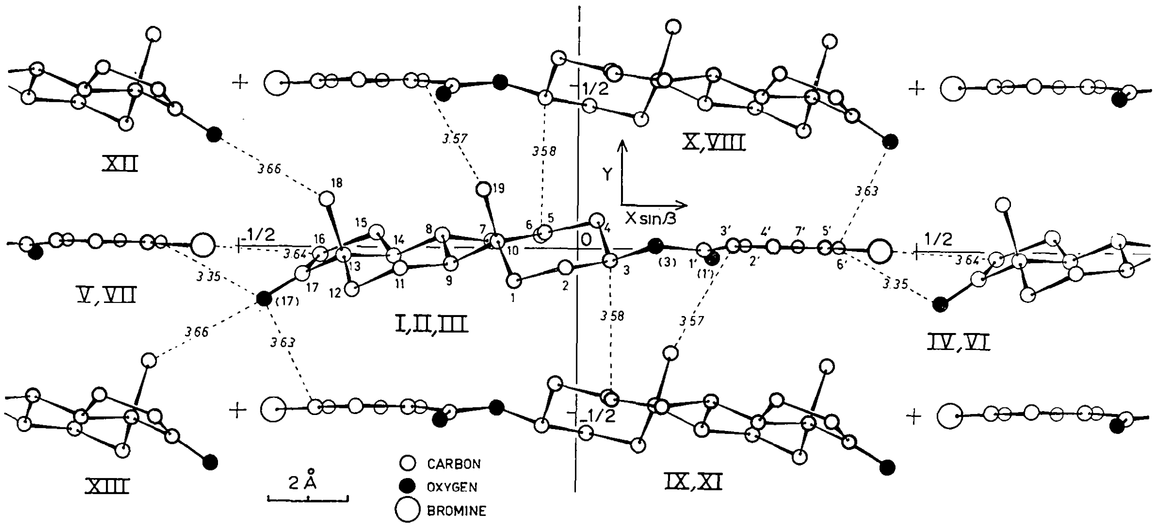


Fig. 6. Projection of BPBA along the *c* axis. The roman numbers are explained in the text. Dotted lines indicate intermolecular distances (Å).

ature structure the position of the *p*-bromobenzoyloxy group at $-180\,^\circ$C is shifted with respect to the steroid part over a distance of $+0{\cdot}04$ Å in the $\bar{\mathbf{a}}$ direction. Moreover, this group is also bent about the carboxyl-group to such an extent that the bromine atom is shifted over $+0{\cdot}03$ Å in the $\bar{\mathbf{b}}$ direction. No discrepancies are observed, within the estimated significance, in the individual bond lengths and bond and torsional angles of the carboxyl group.

The preparation of the title compound was carried out by Mr A. M. van der Werf. Programs for the processing of the diffractometer output were designed by Mr R. A. G. de Graaff. Gratefully we acknowledge the assistance of Dr G. C. Verschoor with the diffractometer measurements. We are indebted to Mrs L. Willemsen, who took the Weissenberg photographs, and to Mr R. C. M. de Groot for producing the figures.

All calculations were performed on the IBM 360/50 computer of the Central Computing Laboratory of the University of Leiden.

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